EXHIBIT X

Techniques and Experiments for Organic Chemistry

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CHAPTER 3

Crystallization

When a solid organic compound is prepared in the laboratory or isolated from some natural source, such as leaves, it is almost always impure. A simple technique for the purification of such a solid compound is **crystallization**. The compound is first dissolved in a minimum amount of hot solvent. If insoluble impurities are present, the hot solution is filtered. If the solution is contaminated with colored impurities, it may be treated with decolorizing charcoal and filtered. The hot, saturated solution is finally allowed to cool slowly so that the desired compound crystallizes at a moderate rate. When the crystals are fully formed, they are isolated from the **mother liquor** (the solution) by filtration.

Crystallization is not the same as precipitation. Precipitation is the *rapid* formation of solid material, while crystallization is the *slow* formation of a crystalline solid. If a hot saturated solution is cooled too quickly, then the compound may precipitate instead of crystallizing. A precipitated solute may contain many impurities trapped in the rapidly formed crystal structure. On the other hand, when a solution is allowed to crystallize slowly, impurities tend to be excluded from the crystal structure because the molecules in the crystal lattice are in equilibrium with the molecules in solution. Molecules that are unsuitable for the crystal lattice are likely to return to solution, and only the most suitable molecules are retained in the crystal structure. Because impurities are usually present in low concentration, they remain in solution even when the solution cools.

If an extremely pure compound is desired, the filtered crystals may be subjected to **recrystallization**. Of course, each crystallization results in some loss of the desired compound, which remains dissolved in the mother liquor along with the impurities.

3.1 Solvents for Crystallization

The ideal solvent for the crystallization of a particular compound is one that: (1) does not react with the compound; (2) boils at a temperature that is below the compound's melting point; (3) dissolves a moderately large amount of the compound when hot; (4) dissolves only a small amount of compound when cool; (5) is moderately volatile so that the final crystals can be dried readily; and (6) is nontoxic, nonflammable, and inexpensive. In addition, impurities should be either highly insoluble in the solvent (so that they can be filtered from the hot solution) or else highly soluble, so that they remain in solution during the crystallization. As you might guess, a solvent possessing *all* these attributes does not exist.

The primary consideration in choosing a solvent for crystallizing a compound is that the compound be moderately soluble. Unfortunately, the solubility of a compound in a solvent cannot be predicted with accuracy. Most commonly, the solubility of a specific compound in various solvents is determined by trial and error. General guidelines for predicting solubilities based upon the structures of organic compounds do exist. For example, an *alcohol*, a compound containing the hydroxyl (—OH) group as its functional group, may be soluble in water because it can form hydrogen bonds with water molecules. If an alcohol's molecules are largely hydrocarbon, the alcohol may be insoluble in water, but will probably be soluble in other alcohols, such as ethanol (CH_3CH_2OH). *Carboxylic acids* (compounds containing —CO_2H groups) and *amines* (compounds containing NH_2, $\geq$NH, or $\geqq$N groups) also can form hydrogen bonds and are also generally soluble in polar solvents such as alcohols.

Compounds that are largely hydrocarbon in structure are not soluble in polar solvents because C—C and C—H bonds are not polar. For these compounds, we would choose a nonpolar solvent—for example, low-boiling petroleum ether, which is a mixture of alkanes such as pentane, $CH_3(CH_2)_3CH_3$, and hexane, $CH_3(CH_2)_4CH_3$. Thus, in choosing crystallization solvents, chemists generally follow the rule of thumb: like dissolves like.

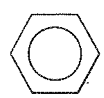
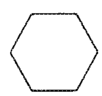
If the best solvent for crystallizing a compound is not known, small portions of the compound can be tested with a variety of likely solvents. The test samples can be recovered by boiling away the solvents. For well-known compounds, however, the best crystallization solvent has already been determined. This information can be found in textbooks, handbooks, and chemical journals. In this book, the crystallization solvent to be used is often specified. Table 3.1 lists some common crystallization solvents.

A. Solvent Pairs

Ideally, a compound to be crystallized should be soluble in the hot solvent, but insoluble in the cold solvent. When a proper solvent cannot be found, a chemist may use a **solvent pair**. A solvent pair is simply two miscible liquids, chosen so that one liquid dissolves the compound readily and the other does not.

For example, many polar organic compounds are highly soluble in ethanol, but insoluble in water. Such a compound is dissolved in a moderate amount of hot ethanol; then water is added dropwise until the solution becomes turbid, or cloudy. A few drops of ethanol are then added to redissolve the precipitating

Table 3.1 *Some common crystallization solvents*

Name	*Structure*	*Bp (°C)*	*Miscibility with water*	*Comments*
water	H_2O	100	—	—
methanol	CH_3OH	65	yes	flammable, toxic
ethanol (95%)	CH_3CH_2OH	78	yes	flammable
acetone (propanone)	$(CH_3)_2C{=}O$	56	yes	flammable
ethyl acetate	$CH_3CO_2CH_2CH_3$	77	no	flammable
carbon tetrachloride (tetrachloro-methane)	CCl_4	77	no	toxic
chloroform (trichloromethane)	$CHCl_3$	61	no	toxic
methylene chloride (dichloromethane)	CH_2Cl_2	41	no	—
diethyl ether (ethyl ether, ether)	$(CH_3CH_2)_2O$	35	no	highly flammable
benzene		80	no	flammable, toxic, carcinogenic, freezes at 5°
cyclohexane		81	no	flammable, freezes at 6.5°
petroleum ether[a]	C_nH_{2n+2}	30–60	no	flammable
ligroin[b]	C_nH_{2n+2}	—	no	flammable

[a] A mixture of alkanes and not a true ether.
[b] A mixture of alkanes boiling at 60–90°, 90–150°, or other specified temperature range. Ligroin is occasionally referred to as "high-boiling petroleum ether."

compound. The resulting ethanol–water solution is a saturated solution and may be allowed to cool slowly for crystallization to occur. Table 3.2 lists some common solvent pairs.

3.2 Safety Using Solvents

Most organic solvents are flammable, toxic, or both. In Table 3.1, we have indicated the most highly flammable and the most highly toxic ones. Because crystallization involves heating solvents to their boiling points, caution must always

Table 3.2 *Some common solvent pairs for crystallization*

methanol–water	diethyl ether–methanol
ethanol–water	diethyl ether–acetone
acetone–water	diethyl ether–petroleum ether
benzene–ligroin	methanol–dichloromethane

be exercised. Solvent fumes should not be sniffed. Toxic solvents should be boiled only in a hood.

A Bunsen burner should be used only for aqueous solutions—and only when no flammable solvents are being used in the vicinity. Some hot plate surfaces are also capable of igniting flammable solvents. The safest heat source for heating a solvent, especially good for low-boiling solvents, is the steam bath. Section 1.3C describes its use.

Boiling chips, or **boiling stones**, should be used when a solvent is brought to a boil, unless the liquid can be constantly stirred or swirled. Boiling chips are small porous stones of calcium carbonate or silicon carbide that contain trapped air. When the chips are heated in a solvent, they release tiny air bubbles, which ensure even boiling. Without boiling chips, part of the solvent may become superheated and boil in spurts, a process called **bumping**. (Bumping is likely to result in part of the solution splashing out of the flask.)

In most cases, two or three boiling chips are all that are necessary to prevent bumping. *Boiling chips should never be added to a hot solution*! If a solution is at or near its boiling point when boiling chips are added, it is almost a certainty that the solution will boil out of the flask.

Boiling chips will maintain their function throughout a long boiling period, but, once they are used and cooled, the pores fill with liquid and lose their ability to release air bubbles. Therefore, fresh boiling chips should be used each time a solution is heated.

Problems

3.1 The proper procedure in crystallization is to allow the hot solution to cool to room temperature, then to chill the solution in an ice bath. Why do we not simply chill the hot solution in an ice bath initially?

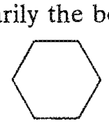
3.2 Each of the following compounds, A–C, is equally soluble in the three solvents listed. In each case, which solvent would you choose? Give reasons for your answer. (More than one answer may be correct.)

(a) Compound A: benzene, acetone, or chloroform
(b) Compound B: carbon tetrachloride, dichloromethane, or ethyl acetate
(c) Compound C: methanol, ethanol, or water

3.3 Which of the following solvents could *not* be used as solvent pairs for crystallization?

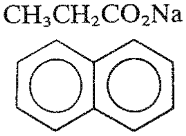
(a) ligroin and water
(b) chloroform and diethyl ether
(c) acetone and methanol

3.4 From the following lists of organic compounds (on the left) and solvents (on the right), choose the solvent in which each solid is likely to be *most soluble* (not necessarily the best crystallization solvent).

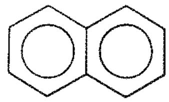
(a)  (1) H_2O

(b) $CH_3(CH_2)_4CH_2OH$ (2) CH_3CH_2OH

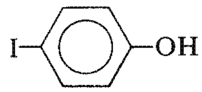
(c) $CH_3CH_2CO_2Na$ (3) petroleum ether

(d) 

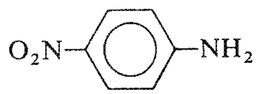
3.5 Using Tables 3.1 and 3.2 (page 38), suggest possible crystallization solvents for the following compounds:

(a) naphthalene,  (mp 80°)

(b) succinic acid, $\mathrm{HO\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}OH}$ (mp 188°)

(c) *p*-iodophenol, 

(mp 94°)

(d) *p*-nitroaniline, 

(mp 148°)

3.6 Draw structures that illustrate the two ways hydrogen bonding can occur between (a) water and methanol, CH_3OH; (b) water and diethylamine, $(CH_3CH_2)_2NH$; (c) water and acetic acid, CH_3CO_2H. (There are more than two correct answers in c.)

»»» EXPERIMENT 3.1 «««

Crystallization of Benzoic Acid and an Unknown

Discussion

The basic steps in the crystallization of an organic solid were summarized in the brief description at the start of this chapter. In this section, we will discuss each of the steps in more detail, along with the techniques that are used to carry out each procedure.

Steps in Crystallization

1) *Dissolving the compound.* The first step in crystallization is dissolving the compound in a *minimum amount* of the appropriate solvent in an Erlenmeyer flask. An Erlenmeyer flask is used instead of a beaker or other container because the solution is less likely to slosh out and dust is less likely to get in; also, an Erlenmeyer flask can be corked and stored in your locker.

Pulverize a lumpy solid with a spatula to speed its dissolving. To ensure that a minimum amount of solvent is used, add the solvent in small portions, and heat the mixture with constant stirring or swirling. As soon as the compound dissolves, examine the solution for insoluble impurities. If these are discovered, filter the hot solution before the compound begins to crystallize.

This filtration is not necessary and is, in fact, undesirable if the solution looks clear and clean. If the solution appears to be contaminated with colored impurities, decolorizing charcoal may be added at this time. The use of decolorizing charcoal is discussed on page 50.

2) *Filtering insoluble impurities.* Filtering a hot, saturated solution inevitably results in cooling and in evaporation of some of the solvent. Therefore, a premature crystallization of the compound on the filter paper and in the funnel may be observed. A few precautions can minimize this premature crystallization.

Before filtering, add a little extra solvent (about 5–10% of the total volume) to the hot solution, and keep the solution hot while the filtration apparatus is being prepared. Preheat the funnel by resting it on the neck of the flask containing the hot solution. A stemless or short-stemmed funnel is convenient for filtering the hot solution because premature crystals may clog the stem of a long-stemmed funnel.

Filter the hot solution through either a plug of glass wool or filter paper. **Fluted filter paper** is preferred to folded filter paper because the increased surface area of the fluted paper allows the filtration to proceed more rapidly. Figure 3.1 shows how to prepare a piece of fluted filter paper. Filter paper is rated by its porosity. For hot filtration, a porous paper, such as Whatman's No. 1 or No. 4, should be used. (Do not use Whatman's No. 5 or No. 6 papers, which have slow filter speeds.)

Heat the empty receiving flask (another Erlenmeyer flask), which will be the actual flask used for the crystallization, on a steam bath or with hot water, and then place the funnel and fluted filter paper in the neck. Figure 3.2 shows two ways in which the funnel can be supported slightly away from the lip of the filtration flask to create an air space, which prevents a liquid "seal" from blocking the flow of air and solvent fumes.

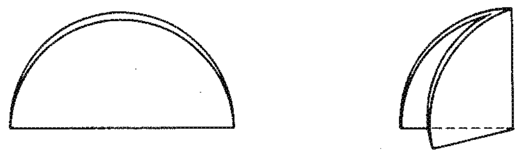
During the filtration, keep both flasks hot on a steam bath or hot plate. To keep the solution hot, pour only small amounts into the filter paper (instead of filling the filter paper to the brim). If a flammable solvent and a hot plate are used, move the flasks away from the hot plate when pouring so that solvent vapors do not flow over the heating element. Wrap the flask containing the hot solution in a towel or hold it in a clamp while pouring, and avoid the hot fumes that flow out of the flask.

If crystallization occurs in the funnel, the crystals can often be removed by heating the receiving flask to boiling with the funnel still on it; solvent condensing in the funnel may dissolve the crystals and carry them back to the filtered solution. Alternatively, the solid can be washed into the flask with a little hot solvent.

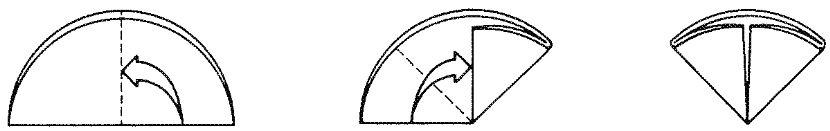
After all of the hot solution has been filtered, wash the original flask with a small amount of hot solvent and pour this solvent through the filter paper into the receiving flask to transfer the final traces of the desired compound. Two washings may be necessary; however, use a minimum amount of solvent.

The crystallization flask should contain a hot, clear, saturated solution of the compound. Boil away excess solvent at this time. (Remember to use the hood for a toxic solvent and stay away from flames with a flammable solvent.)

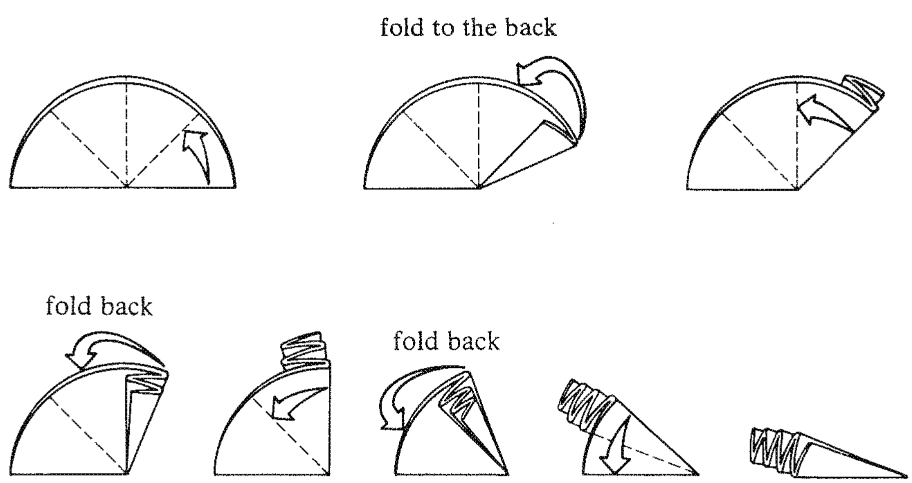
Step 1. Fold the paper in half, then in quarters, creasing the folds as you proceed. However, do not crease the very center of the paper (the point), which might become weakened.



Step 2. Open the quarters to a half-sized piece, and then fold the edges in to the centerfold.



Step 3. Open the paper again to a half-sized piece, then accordian-pleat, using the existing fold lines as guides. (Again, do not crease the center of the paper.)



Step 4. Crease the folds (except at the point), then open the filter paper and place it in an appropriately sized funnel.

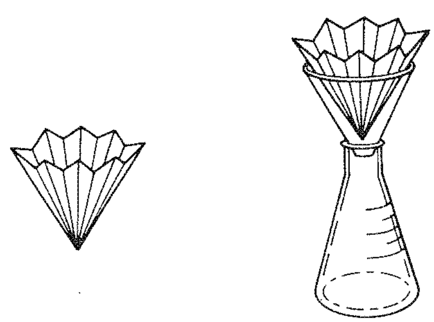


Figure 3.1 *How to prepare fluted filter paper.*

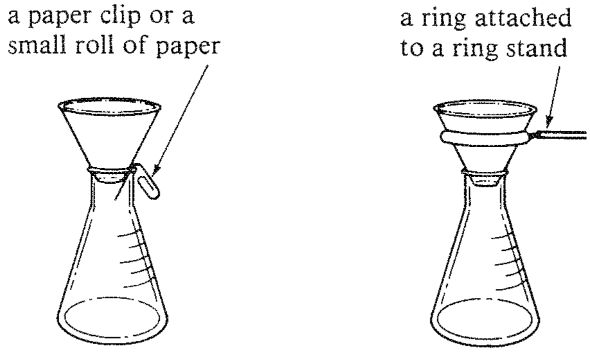


Figure 3.2 *Ways to create an air space between a funnel and an Erlenmeyer flask.*

If the hot solution starts to crystallize, reheat it to dissolve the crystals. If so much solvent has evaporated that the crystals will not dissolve, add a small additional amount of solvent to the flask.

3) *Crystallizing the compound.* Cover the flask containing the hot, saturated solution with a watch glass or inverted beaker to prevent solvent evaporation and dust contamination. Then, set the flask aside where it can remain undisturbed (no jostling or bumping, which will induce precipitation rather than crystallization) for an hour or several hours. If the flask must sit for several days, allow it to cool to room temperature, then stopper it with a cork (not a rubber stopper if an organic solvent was used) to prevent solvent evaporation.

Sometimes a hot solution cools to room temperature with no crystallization occurring. In such a case, your first question should be, "Is the solution *supersaturated*?" Often, crystallization can be induced in a supersaturated solution by scratching the inside of the flask up and down at the surface of the solution with a glass rod. The scratching of the glass on glass is thought to release microcrystals of glass, which serve as a template for crystal growth. If scratching the flask does not start the crystallization, a **seed crystal** may be added. This is a small crystal of the original material set aside for just this purpose; it provides a nucleus, or template, upon which other crystals can grow. Sometimes a seed crystal can be obtained from the glass rod used for scratching, after the solvent has evaporated from it. Allowing a few drops of solution to evaporate on a watch glass may also produce seed crystals. After addition of the seed crystal, set the flask aside for crystallization to proceed.

If scratching and seeding do not produce crystals, your next question should be, "Did I use too much solvent?" If more than the minimum amount of solvent was used in the earlier steps, then the excess must be boiled away and the flask set aside again to crystallize. Unless the solid begins to separate, reducing the volume of the solution by one third may result in the desired saturated solution.

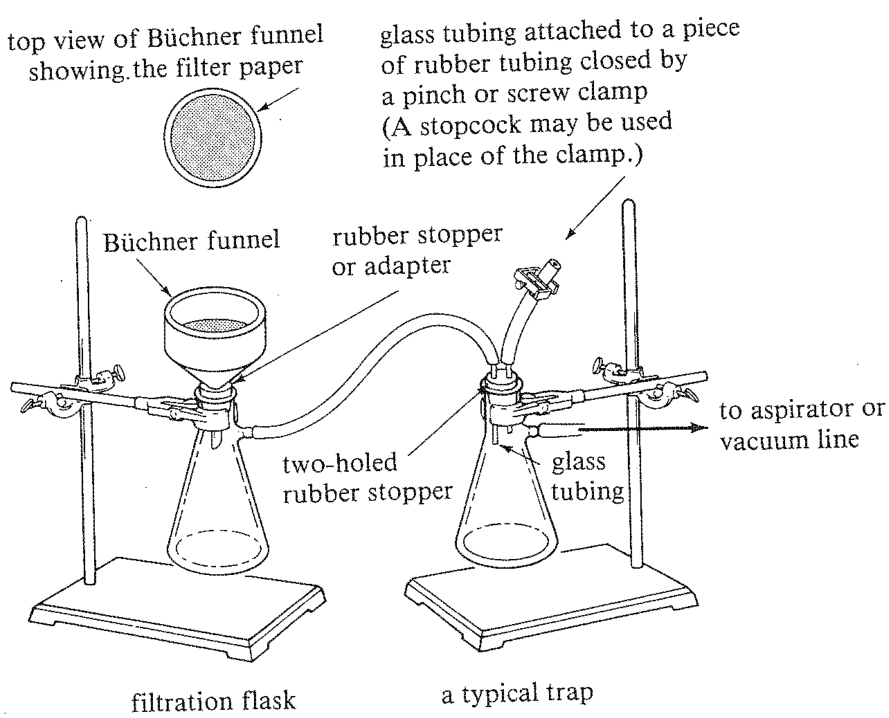
Another problem encountered in crystallization is **oiling out**: instead of crystals appearing, an oily liquid separates from solution. A compound may oil out if its melting point is lower than the boiling point of the solvent. A very impure compound may oil out because the impurities depress its melting point.

The formation of an oil is not selective, as is crystallization; therefore, the oil (even if it solidifies) is probably not a pure compound. Reheat a mixture that has oiled out to dissolve the oil (add more solvent if necessary) and then allow the solution to cool slowly, perhaps adding a seed crystal or scratching with a glass rod.

If these techniques do not prevent oiling out, allow the oil to solidify (a seed crystal may be necessary), filter the solid or decant (pour) the solvent away, and attempt to crystallize the solid with fresh solvent. Enough impurities may have been removed in the first attempted crystallization that the second one will proceed smoothly. If the substance has a low melting point, a lower-boiling solvent may be necessary. Alternatively, keeping the temperature of the solvent below the melting point of the solute may help prevent oiling out.

4) *Isolating the crystals.* Crystals are separated from their mother liquor by filtration. Chilling the mixture in an ice-water bath before filtration will increase the yield of crystals. The standard filtration process used is called **vacuum** or **suction filtration.**

Vacuum filtration apparatus. Vacuum filtration has the advantage of being much faster than gravity filtration (simple filtration through filter paper and funnel). It has the disadvantage of requiring more equipment. Figure 3.3 shows the physical setup required for vacuum filtration. The trap is necessary regardless of whether a water aspirator or a centralized vacuum system is used.



Note: Flasks and tubing are heavy-walled.

Figure 3.3 A vacuum filtration apparatus.

The purpose of this trap is two-fold: (a) Any solution accidentally sucked into the vacuum line will be caught in the trap. (b) Water from an aspirator sometimes backs up into the vacuum line. With a trap, this water will be caught before it contaminates the mother liquor in the filtration flask.

Heavy-walled vacuum tubing is used for connections because ordinary tubing collapses when vacuum is applied. All flasks should be clamped to ring stands. The filter flask, especially, should be firmly clamped because it usually becomes top-heavy when a Büchner funnel and vacuum line are connected to it.

Attach the Büchner funnel or Hirsch funnel to the filter flask with a rubber adapter or a one-holed rubber stopper (best) so that the connection will be airtight when vacuum is applied. Place a medium- or slow-speed filter paper (such as Whatman's No. 2, 5, or 6) on the perforated surface of the funnel. (A fast-speed, porous filter paper allows finely divided solids to pass through under vacuum.) The filter paper must lie flat and not curl up at the sides, yet it must cover all the holes. When the vacuum is applied, the filter paper is pulled snugly to the flat surface of the funnel by suction. To ensure no leakage around the edges, moisten the filter paper with the solvent before applying vacuum.

Water aspirator. Many laboratories are equipped with **water aspirators**, devices that attach to faucets and develop a vacuum through a side tube when water flows through the main tube. A large beaker in the sink under the water outlet minimizes splashing. Because aspirators are easily plugged, they should be checked before each use. Turn the water on *full force* and hold your finger on the vacuum hole to feel the suction before attaching your filtration apparatus.

As we have mentioned, an aspirator can "back up." A slight decrease in water pressure can cause the vacuum in the filtration apparatus to pull water into the apparatus. If you see water entering the trap, break the vacuum by opening the stopcock or clamp on the trap to save your mother liquor from the influx of tap water.

The actual filtration. For nonvolatile solvents like water, apply the vacuum and pour the crystallization mixture into the Büchner funnel at such a rate that the bottom of the funnel is always covered with some solution. If the solvent is volatile, keep the vacuum off when pouring the first portion of the mixture into the funnel; then apply the vacuum. When the vacuum is applied, the mother liquor is literally sucked through the filter paper into the filter flask while the crystals remain on the filter paper. When the mother liquor ceases to flow from the funnel stem, release the vacuum by opening the stopcock on the trap, then turn off the aspirator or vacuum line.

Washing. To wash the contaminating mother liquor from the crystals, transfer the crystal mass, or filter cake, to a small beaker, using a spatula to loosen, remove, and scrape the filter paper. Place fresh filter paper in the Büchner funnel, stir the crystals with a small amount of *chilled* solvent, then immediately refilter. Small amounts of crystals may be washed right in the funnel on the original filter paper. This procedure is not recommended because the wet filter paper may tear when you stir the wash solvent into the crystals and because this type of washing is not as thorough as a beaker washing.

Remove excess solvent from the crystals by putting a fresh piece of filter paper *on top of the crystals* still in the funnel and pressing this filter paper down firmly and all over with a cork. Keep the vacuum on during this pressing. When as much solvent has been pressed out of the filter cake as possible, leave the vacuum running for another minute or so. The air pulled through the filter cake will remove even more solvent. Then, open the trap clamp, turn off the vacuum, remove the Büchner funnel, and disconnect the filter-flask assembly from the vacuum line. Using a spatula, pry the filter cake from the funnel for drying.

Do not discard the mother liquor (in the filter flask), but place it in a corked Erlenmeyer flask until the completion of the experiment. The reason for saving the mother liquor is that it may still contain a substantial amount of the desired compound.

5) *Drying the crystals*. The filter cake removed from the Büchner funnel still contains an appreciable amount of solvent. The crystals must be dried thoroughly before they can be weighed or before a melting point can be taken. (Why?)

There are many methods for drying crystals. The simplest is *air-drying*, in which the crystals (with any lumps crushed) are spread out on a watch glass or large piece of filter paper and allowed to dry. Air-drying is sometimes slow, especially if water or some other high-boiling solvent was used. Unless the crystals are partially covered, they can collect dust. Another watch glass or a beaker, propped on corks to allow air to get to the crystals, may be used as a cover. For a melting-point determination, a few crystals may be removed from the mass and allowed to air-dry on a separate uncovered watch glass. If a compound is hygroscopic (attracts water from the air), it cannot be air-dried.

A **desiccator** may be used for drying a water-crystallized or hygroscopic compound. A desiccant (drying agent) such as anhydrous calcium chloride is placed in the bottom of the desiccator; the porcelain shelf is inserted; then a watch glass or beaker holding the crystals is placed on the shelf. When the cover is in place, the desiccant attracts water from the atmosphere in the desiccator as the water evaporates from the crystals. Some desiccators can be evacuated, thus speeding up the evaporation of any solvent.

6) *The second crop*. The mother liquor from a crystallization may still contain in solution a large amount of the desired compound. In many cases, another batch of crystals, called the **second crop**, can be obtained from this mother liquor. This can be accomplished by boiling away some of the solvent from the mother liquor and allowing it to cool and crystallize as for the first crop of crystals. A seed crystal added to the cooled solution may help start the crystallization process. The second crop of crystals is rarely as pure as the first crop because the impurities have been concentrated in the mother liquor. The purity of the second crop can be improved by recrystallization of these impure crystals with fresh solvent.

Additional crops can sometimes be harvested from each mother liquor by repeating the process described above. Each successive crop will be less pure than the preceding crop. For this reason, only one or two crops are usually taken.

Experimental

EQUIPMENT:

250-mL (or larger) beaker
two 250-mL Erlenmeyer flasks
filter paper (Whatman's No. 1 or 4 and No. 2, 5, or 6)
hot plate and water bath
ice bath
melting-point apparatus
short-stemmed funnel
spatula
6–8 test tubes
vacuum filtration assembly

CHEMICALS:

impure benzoic acid, 5 g
individual unknown,* 2.0 g
solvents: 95% ethanol, acetone, dichloromethane (methylene chloride), petroleum ether (30–60°), ligroin (60–90°)

TIME REQUIRED: 2 hours for Part A, $1\frac{1}{2}$ hours for Part B, plus overnight drying of the crystals and melting-point determinations. (The time required will be shorter if a burner is used in Part A instead of a hot plate.)

STOPPING POINTS: while any solution is crystallizing or while the crystals are drying

>>>> **SAFETY NOTE** Part A of this experiment includes the heating of water, while Part B includes the use of flammable solvents. It is recommended that a *hot plate* be used for the crystallizations from water. If a burner is used, it is imperative that you and your neighbors coordinate your activities so that burners and flammable solvents are *not* used at the same time.

PROCEDURE

A. Crystallization of Benzoic Acid from Water

Weigh approximately 5.0 g of crude benzoic acid into a 250-mL Erlenmeyer flask. Record the weight of the benzoic acid to the nearest 0.1 g.

Heat 150–200 mL of distilled water to boiling in a beaker on a hot plate. Because you will later need a warmed flask and funnel, add 10 mL of distilled water to another 250-mL flask, place a short-stemmed funnel in the neck of the flask, and heat to a gentle boil (adding more water, if necessary).

Flute a piece of porous filter paper as shown in Figure 3.1, page 42. Add 100 mL of distilled water and 2–3 boiling chips to the benzoic acid, and

* Suggestions for unknowns are listed in the instructor's guide.

bring the mixture to a boil. Since the benzoic acid used in this experiment contains insoluble impurities, most, but not all, of the solid should go into solution. If necessary, add more water (up to 25 mL) to dissolve the benzoic acid. Filter the hot solution through the fluted filter paper into the heated flask (emptied of the hot water).

After the filtration is complete, wash the original flask with 5 mL of boiling water and pour this wash water through the filter paper. Then wash the filter paper with an additional 5 mL of boiling water.

To remove excess water from the filtrate, add 2–3 fresh boiling chips, and boil the solution until its volume is about 100 mL. Then, cover the flask with an inverted beaker and place the flask on the bench top or in your locker to cool slowly to room temperature.

While the solution is cooling, equip a filter flask with a Büchner funnel and a water trap (see Figure 3.3, page 44). Then, vacuum-filter the crystals, wash the filter cake with ice-cold water as described in the discussion, and refilter. Transfer the filter paper with the crystals onto a piece of fresh filter paper and allow the crystals to air-dry overnight or longer.

Weigh the dry crystals and calculate the per cent recovery. (In your calculation, ignore the presence of impurities; assume that all the material placed in the Erlenmeyer flask was benzoic acid.) A 65% recovery is typical.

Determine the melting point of the crystallized benzoic acid. Enter all pertinent data in your notebook, place the benzoic acid in a properly labeled vial, and turn in the vial to your instructor.

If desired, a second crop (about 5% recovery) of benzoic acid can be obtained from the water filtrate. To obtain a second crop, transfer the mother liquor to an Erlenmeyer flask, boil on a hot plate to reduce the volume by about one third, cool, filter the crystals with vacuum, and air-dry them. Do not combine the second crop with the first crop (why not?), but determine its weight and melting point, then hand it in to your instructor in a vial labeled as the "second crop." Report the per cent recovery as two values: per cent recovery for the first crop and total per cent recovery (first and second crops).

B. Crystallization of an Unknown

Obtain an unknown (CAUTION: possibly toxic) from your instructor, and record its number in your notebook. Use the following procedure to choose a suitable crystallization solvent.

Weigh exactly 0.10 g of the unknown into a small test tube. Pipet exactly 1.0 mL of water into another test tube. Use these two test tubes as references for estimating 0.10 g of unknown and 1.0 mL of solvent for the other test tubes.

Place an estimated 0.10 g of the unknown in each of six test tubes, and add 1.0 mL of solvent to each. The following solvents should be tried: water, 95% ethanol, acetone, dichloromethane, petroleum ether (30–60°), and ligroin (60–90°). The boiling points of these solvents are listed in Table 3.1, page 38. (CAUTION: Most of these solvents are flammable; all burners should be extinguished!) Stir each sample, and determine the solubility of your unknown

in each solvent at room temperature. Place the test tubes in a beaker of boiling water on a hot plate, and again note the solubilities. (Some of the unknowns may contain insoluble impurities even though the unknown compound itself dissolves.)

Return the test tubes to a rack and allow them to cool to room temperature. Finally, place the test tubes in an ice bath. Record your observations.

From the preceding tests, choose the best solvent (or solvent pair) for the crystallization of the unknown, then weigh and crystallize the remainder of your unknown sample. Air-dry the crystals overnight, then determine the per cent recovery and melting point. Hand in the dried crystals in a labeled vial to your instructor.

Problems

3.7 Give reasons for each of the following experimental techniques used in crystallization:

(a) A hot crystallization solution is not filtered unless absolutely necessary.

(b) An Erlenmeyer flask containing a hot solution is not tightly stoppered to prevent solvent loss during cooling.

(c) The suction of a vacuum filtration apparatus is broken before the vacuum is turned off.

(d) Vacuum filtration is avoided when crystals are isolated from a very volatile solvent.

(e) Carborundum (silicon carbide) boiling chips are better than calcium carbonate chips in the crystallization of an unknown.

3.8 A procedure suggests using 25 mL of solvent for crystallizing 5.0 g of a compound. What size flask would you choose to crystallize 30 g?

3.9 How would you recover the solid unknown that was used to determine the correct solvent for crystallization?

3.10 A chemist crystallizes 17.5 g of a solid and isolates 10.2 g as the first crop and 3.2 g as the second crop.

(a) What is the per cent recovery in the first crop?

(b) What is the total per cent recovery?

3.11 A student carried out a crystallization from water and obtained a 120% recovery. How could this happen?

3.12 A student crystallized a compound from benzene and observed only a few crystals when the solution cooled to room temperature. To increase the yield of crystals, the student chilled the mixture in an ice-water bath. The chilling greatly increased the quantity of solid material in the flask. Yet, when the student filtered these crystals with vacuum, only a few crystals remained on the filter paper. Explain this student's observations.

3.13 At 0°, the solubility of benzoic acid is 0.02 g/100 mL of water. Assume that you carry out Experiment 3.1A using 5.00 g of pure benzoic acid, boiling the solution down to exactly 100.0 mL, then chilling the solution to 0°.

(a) What is the theoretical maximum per cent recovery in the first crop?

(b) If you boiled the mother liquor down to 50 mL and collected a second crop, what is the theoretical maximum per cent recovery (total)?

EXPERIMENT 3.2

(SUPPLEMENTAL)

Crystallization of Acetanilide Using Decolorizing Charcoal

Discussion

Frequently, small amounts of colored compounds and tarry (long-chain, or polymeric) compounds are found as colored impurities in colorless organic compounds. These colored impurities can cause the crystallization solution and even the final crystals to have a tinge of color. These impurities can be removed with **decolorizing charcoal** (also called *activated charcoal* or *activated carbon*). The fine particles of carbon in decolorizing charcoal have a large surface area and adsorb organic compounds, especially colored and polymeric compounds.

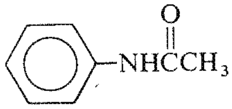
The decolorizing charcoal is added to the initial crystallization solution after the impure solid has been dissolved. *Never* add decolorizing charcoal to a solution near its boiling point! The fine particles act like thousands of tiny boiling chips and will cause a hot solution to boil over. Therefore, always allow a hot solution to cool for 3–4 minutes before adding the charcoal.

Only a small amount of decolorizing charcoal should be used: a "pinch" (0.1–0.5 g) on the end of a spatula is sufficient for most purposes. It is always better to err by adding too little charcoal than too much, because the particles of carbon can adsorb the desired compound as well as impurities.

After the carbon is added, the mixture should be swirled a few times, then *carefully* reheated. (Boiling solutions containing decolorizing charcoal have a tendency to froth.) The hot mixture is then filtered through fluted filter paper as was described on page 42.

Because decolorizing charcoal is messy, and because its use always results in the loss of some of the compound being crystallized, decolorizing is carried out only when necessary and not as a routine procedure. If the use of decolorizing charcoal is being considered, it is generally advisable to first test an aliquot of the solution.

In this experiment, you will use decolorizing charcoal to decolorize acetanilide contaminated with the dye methylene blue.



acetanilide

Experimental

EQUIPMENT:

three 250-mL Erlenmeyer flasks
filter paper (Whatman's No. 1 or 4, and No. 2, 5, or 6)
hot plate
ice bath
melting-point apparatus
short-stemmed funnel
spatula
vacuum filtration assembly

CHEMICALS:

acetanilide contaminated with 0.1% methylene blue, 10 g
decolorizing charcoal, 0.1 g (Two 0.1-g quantities may be needed.)

TIME REQUIRED: $2\frac{1}{2}$ hours plus overnight drying and melting-point determination.

STOPPING POINTS: While any solution is crystallizing or while the crystals are drying.

»»» **SAFETY NOTE** Do *not* add decolorizing charcoal to a hot solution. Avoid getting decolorizing charcoal on your skin or clothing because it is difficult to wash way.

PROCEDURE

Weigh 5.0 g of contaminated acetanilide (see Experimental Note) in a 250-mL Erlenmeyer flask, add 100 mL of water, add 2–3 boiling chips, and boil the mixture until the acetanilide dissolves. (Be sure that it has dissolved and not simply melted.) Allow the acetanilide to crystallize, chill the flask in an ice bath, and filter the crystals with vacuum.

Weigh another 5.0-g sample of contaminated acetanilide into a clean flask, and dissolve this sample in 100 mL of boiling water as before. Remove the flask from the burner, then add 30 mL of cold water and about 0.1 g of decolorizing charcoal. Bring the mixture to a boil, but be prepared to remove the flask from the hot plate if it froths. Boil the mixture for 1–2 minutes.

Filter the hot mixture by gravity, using an additional 20 mL of hot water to wash the Erlenmeyer flask and the filter paper. The total volume of the filtrate should be around 150 mL. (If the solution is still blue, repeat the treatment with decolorizing charcoal.) Add 2–3 boiling chips and boil the solution down to 100 mL. Allow the flask to stand until crystals have formed, then cool it in an ice bath. Filter the crystals with vacuum, and allow both sets of crystals to air-dry at least overnight. Weigh the samples and determine their melting points simultaneously after looking up the melting point in the *Handbook of Chemistry and Physics*. Compare the appearance and melting

points of the two samples, and record your observations and conclusions in your notebook. Turn in both samples (in properly labeled vials) to your instructor.

EXPERIMENTAL NOTE

The success of this experiment depends upon the amount of methylene blue used as an impurity and the activity of the decolorizing charcoal. It is assumed that the storeroom has balanced the two variables.

Problems

3.14 Explain why: (a) excess solvent is used when decolorizing a solution with decolorizing charcoal; (b) a crystallization solution is heated *after* the decolorizing charcoal is added.

3.15 How could you determine the minimum amount of decolorizing charcoal needed to decolorize a crystallization solution?

3.16 The solubility of acetanilide in hot water (5.5 g/100 mL at 100°) is not very great, and its solubility in cold water (0.53 g/100 mL at 0°) is significant. What would be the maximum theoretical per cent recovery (first crop only) from the crystallization of 5.0 g of acetanilide from 100 mL of water (assuming the solution is chilled to 0°)?